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## (54) ORGANIC POSITIVE CHARACTERISTIC THERMISTOR AND ITS MANUFACTURE

(57)Abstract:

PROBLEM TO BE SOLVED: To improve characteristic stability by performing the crosslinking treatment with a mixture of a thermoplastic macromolecular matrix, a low-molecular organic compound whose melting point is within a specific temperature range, and a conductive particle with a spike-shaped projection with vinyl group or (meta)acryloyl group and a silane coupling agent of alkoxy group.

SOLUTION: An organic positive characteristic thermistor contains a thermoplastic macromolecular matrix, a low-molecular organic compound whose melting point is 40°C or higher and less than 100°C, and a conductive particle with a spike-shaped projection, and performs the crosslinking treatment of the mixture with a silane coupling agent with a vinyl group or a (meth)acryloyl group, and an alkoxy group. Then, polyalkyl acrylate, polyolefin, or the like is used for the thermoplastic macromolecular matrix. The low-molecular organic compound is a crystallizability substance with a molecular weight of up to approximately 1,000 and oil wax is used for it. Also, an Ni power where a plurality of conical projections exist in one particle or the like is used for the conductive particle with a spike-shaped projection.

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**CLAIMS**

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[Claim(s)]

[Claim 1] The organic positive thermistor with which a thermoplastic macromolecule matrix and the melting point carried out bridge formation processing of such mixture including the conductive particle which has the projection of a less than 100-degree C low-molecular organic compound 40 degrees C or more and the letter of a spike by the silane system coupling agent which has a vinyl group or (meta) an acryloyl radical, and an alkoxy group.

[Claim 2] The organic positive thermistor of claim 1 whose weight average molecular weight of said low-molecular organic compound is 1,000 or less.

[Claim 3] The organic positive thermistor of claims 1 or 2 said whose low-molecular organic compounds are petroleum system waxes.

[Claim 4] One organic positive thermistor of claims 1-3 with which the conductive particle which has the projection of said letter of a spike stands in a row in the shape of a chain.

[Claim 5] One organic positive thermistor of claims 1-4 said whose thermoplastic macromolecule matrices are polyolefine.

[Claim 6] The organic positive thermistor of claim 5 said whose polyolefine is high density polyethylene.

[Claim 7] The organic positive thermistor of claim 6 whose melt flow rates of said high density polyethylene are 3.0g / 10 min or less.

[Claim 8] One organic positive thermistor of claims 1-7 said whose silane system coupling agents are vinyltrimetoxysilane or vinyltriethoxysilane.

[Claim 9] One organic positive thermistor of claims 1-8 whose operating temperature is less than 100 degrees C.

[Claim 10] The manufacture approach of an organic positive thermistor of a thermoplastic macromolecule matrix and the melting point kneading the conductive particle which has the projection of a less than 100-degree C low-molecular organic compound 40 degrees C or more and the letter of a spike, carrying out bridge formation processing of this kneading object by the silane system coupling agent which has a vinyl group or (meta) an acryloyl radical, and an alkoxy group, and obtaining one organic positive thermistor of claims 1-9.

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**DETAILED DESCRIPTION**

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention is used as a thermo sensor or an overcurrent protection component, and relates to the organic positive thermistor which has the PTC (positive temperature coefficient of resistivity) property that resistance increases with a temperature rise.

[0002]

[Description of the Prior Art] In this field, the organic positive thermistor which made the crystalline macromolecule distribute a conductive particle is well-known, and is indicated by the U.S. Pat. No. 3243753 description, the 3351882 description, etc. A crystalline polymer expands with fusion and buildup of resistance is considered for cutting the electric conduction path of a conductive particle.

[0003] An organic positive thermistor can be used for an autogenous regulation mold heating element, an overcurrent protection component, a thermo sensor, etc. As a property required of these, it is mentioned that the room temperature resistance at the time of un-operating is low enough, that room temperature resistance and the rate of a resistance value change at the time of actuation are large enough, and that the resistance value change by repeat actuation is small.

[0004] In order to satisfy such demand characteristics, making low-molecular organic compounds, such as a wax, contain in a macromolecule matrix is proposed. As such an organic positive thermistor, there are a polyisobutylene / paraffin wax / carbon black system (F. Bueche, J.Appl.Phys., 44, 532, 1973), styrene-butadiene rubber / paraffin wax / carbon black system (F. Bueche, J.Polymer Sci., 11, 1319, 1973), and low density polyethylene / paraffin wax / carbon black system (KOhe et al., Jpn.J.Appl.Phys., 10, 99, 1971), for example. Moreover, a self-temperature control heating element, a \*\* style component, etc. using the organic positive thermistor using a low-molecular organic compound are indicated by each official report of JP,62-16523,B, JP,7-109786,B, 7-48396, JP,62-51184,A, 62-51185, 62-51186, 62-51187, JP,1-231284,A, 3-132001, 9-27383, and 9-69410. It is thought that resistance increases by fusion of a low-molecular organic compound in these cases.

[0005] Therefore, as for the advantage when using a low-molecular organic compound, it is mentioned that the standup at the time of generally resistance increasing according to temperature up since degree of crystallinity is high compared with a macromolecule becomes steep. Moreover, although a hysteresis to which the direction of the temperature to which resistance usually decreases from the temperature to which resistance increases at the time of temperature up at the time of a temperature fall becomes low is shown in order that a macromolecule may tend to take a supercooling condition, this hysteresis can be suppressed by using a low-molecular organic compound. Furthermore, if the low-molecular organic compound with which the melting points differ is used, the temperature (operating temperature) to which resistance increases is easily controllable. In the case of a macromolecule, by copolymerizing with the difference in molecular weight or degree of crystallinity, and a comonomer, the melting point can change, operating temperature can be changed, but in that case, since it is accompanied by change of a crystallized state, sufficient PTC property may not be acquired. Especially this tends to become more remarkable when setting operating temperature as less than 100 degrees C.

[0006] In the above-mentioned reference, the example which resistivity (ohm cm) increased by 108 times is shown in Jpn.J.Appl.Phys., and 10, 99 and 1971. However, the resistivity in a room temperature is dramatically high at 104ohm cm, and is not practical using especially an overcurrent protection component or a thermo sensor. Moreover, the range of 10 or less to about 104 times has each increment in the resistance (omega) in

other reference, or resistivity (ohm cm), and it is not sufficiently low. [ of room temperature resistance ]  
 [0007] On the other hand, although many carbon black and graphites had been used as a conductive particle with the conventional organic positive thermistor also including the above-mentioned thing, in order to lower initial resistance, when the fill of carbon black was made [ many ], sufficient resistance rate of change was not acquired, but there was a fault that it was incompatible in low initial resistance and big resistance rate of change. Moreover, although there was also an example which used general metal particles for the conductive particle, it was difficult to reconcile similarly low initial resistance and big resistance rate of change.

[0008] As an approach of solving the above-mentioned fault, the approach using the conductive particle which has the projection of the letter of a spike is indicated by JP,5-47503,A. More specifically, the thing which has the projection of the letter of a spike using the letter nickel powder of a spike as a conductive particle is indicated, using polyvinylidene fluoride as a crystalline giant molecule. Moreover, the thing using nickel of the filament configuration which has the projection of the letter of a spike also on U.S. Pat. No. 5378407 descriptions, and polyolefine, an olefin system copolymer or fluoropolymers is indicated.

[0009] In these things, although the effectiveness of reconciling low initial resistance and a big resistance change improves, the point of a hysteresis is inadequate and it is not suitable for an application like especially a thermo sensor. And the operating temperature of these things is 100 degrees C or more. Although some which are 60-90 degrees C have operating temperature, these have an unstable property by repeat actuation, and it is not practical. When the application as protection components, such as a heater for a rechargeable battery, an electric blanket, the seat, and the sheets for cars, is considered, in the operating temperature of 100 degrees C or more, the danger to the body is large. Considering the safety to the body, operating temperature needs to be less than 100 degrees C. Moreover, although the need of an organic positive thermistor as overcurrent protection components, such as a cellular phone and a personal computer, is high recently, that service temperature is usually about 40-90 degrees C, and 40-degree-C or more less than 100-degree C thermistor is called for for operating temperature also from this field.

[0010] As above, the operating temperature of less than 100 degrees C shows a good property, and, now, the organic positive thermistor with a stable property is not obtained.

[0011] this invention persons have proposed the organic positive thermistor containing the conductive particle which has the projection of a thermoplastic macromolecule matrix, a low-molecular organic compound, and the letter of a spike in a Japanese-Patent-Application-No. No. 350108 [ nine to ] official report. This thing has low room temperature specific resistance enough at  $8 \times 10$  to 2 or less ohm cm, its resistance rate of change at the time of actuation and un-operating is as large as 10 or more figures, and its hysteresis of a temperature-system head curve is still smaller. And the operating temperature is 40 degrees C or more less than 100 degrees C.

[0012] However, this thermistor has inadequate property stability and resistance especially increases it notably under high-humidity/temperature. It originates in the low melting point of a low-molecular organic compound, and low melt viscosity, while repeating melting-coagulation at the time of actuation, the segregation of the low-molecular organic compound of a working substance etc. happens, and this is considered that the distributed condition of a macromolecule matrix, a low-molecular organic compound, and a conductive particle changes, and a property deteriorates. The problem of such property stability is a problem important when using a low-molecular organic compound as a working substance.

[0013]

[Problem(s) to be Solved by the Invention] Sufficiently low room temperature resistance is obtained, the object of this invention has the large resistance rate of change at the time of actuation and un-operating, and operates at less than 100 degrees C, its hysteresis of a temperature-system head curve is small, and adjustment of operating temperature is easy for it, and it is offering an organic positive thermistor with high property stability moreover.

[0014]

[Means for Solving the Problem] Such an object is attained by following this invention.

(1) The organic positive thermistor with which a thermoplastic macromolecule matrix and the melting point carried out bridge formation processing of such mixture including the conductive particle which has the projection of a less than 100-degree C low-molecular organic compound 40 degrees C or more and the letter of a spike by the silane system coupling agent which has a vinyl group or (meta) an acryloyl radical, and an alkoxy group.

(2) The organic positive thermistor of the above (1) whose weight average molecular weight of said low-molecular organic compound is 1,000 or less.

(3) The above (1) said whose low-molecular organic compound is a petroleum system wax, or (2) organic positive thermistors.

(4) One organic positive thermistor of above-mentioned (1) - (3) with which the conductive particle which has the projection of said letter of a spike stands in a row in the shape of a chain.

(5) One organic positive thermistor of above-mentioned (1) - (4) said whose thermoplastic macromolecule matrices are polyolefine.

(6) The organic positive thermistor of the above (5) said whose polyolefine is high density polyethylene.

(7) The organic positive thermistor of the above (6) whose melt flow rates of said high density polyethylene are 3.0g / 10 min or less.

(8) One organic positive thermistor of above-mentioned (1) - (7) said whose silane system coupling agents are vinyltrimetoxysilane or vinyltriethoxysilane.

(9) One organic positive thermistor of above-mentioned (1) - (8) whose operating temperature is less than 100 degrees C.

(10) The manufacture approach of an organic positive thermistor of a thermoplastic macromolecule matrix and the melting point kneading the conductive particle which has the projection of a less than 100-degree C low-molecular organic compound 40 degrees C or more and the letter of a spike, carrying out bridge formation processing of this kneading object by the silane system coupling agent which has a vinyl group or (meta) an acryloyl radical, and an alkoxy group, and obtaining one organic positive thermistor of above-mentioned (1) - (9).

[0015]

[Function] The organic positive thermistor of this invention carries out bridge formation processing of such mixture including the conductive particle to which a thermoplastic macromolecule matrix and the melting point have the projection of a less than 100-degree C low-molecular organic compound 40 degrees C or more and the letter of a spike by the silane system coupling agent which has a vinyl group or (meta) an acryloyl radical, and an alkoxy group.

[0016] By this invention, by using the conductive particle which has the projection of the letter of a spike, tunnel current becomes easy to flow for the configuration, and low room temperature resistance is obtained as compared with a spherical conductive particle. Moreover, since it is large compared with what has spherical spacing between conductive particles, a big resistance change is obtained at the time of actuation.

[0017] Moreover, since the thermoplastic macromolecule matrix and the PTC property that make polyolefine contain a low-molecular organic compound preferably, and resistance increases with a temperature rise by fusion of this low-molecular organic compound are made to discover, compared with the case where only a macromolecule matrix is used, the hysteresis of a temperature-system head curve becomes small. Moreover, operating temperature can be easily adjusted by using the low-molecular organic compound with which the melting points differ compared with the case where operating temperature is adjusted using melting point change of a macromolecule etc. And in this invention, the melting point makes operating temperature less than 100 degrees C by using low-molecular 40-degree-C or more less than 100-degree C organic compound for a working substance.

[0018] And the property stability at the time of repeat actuation improves remarkably at the time of preservation by carrying out bridge formation processing of the mixture of the conductive particle which has the projection of a thermoplastic macromolecule matrix, a low-molecular organic compound, and the letter of a spike by the silane system coupling agent which has a vinyl group or (meta) an acryloyl radical, and an alkoxy group.

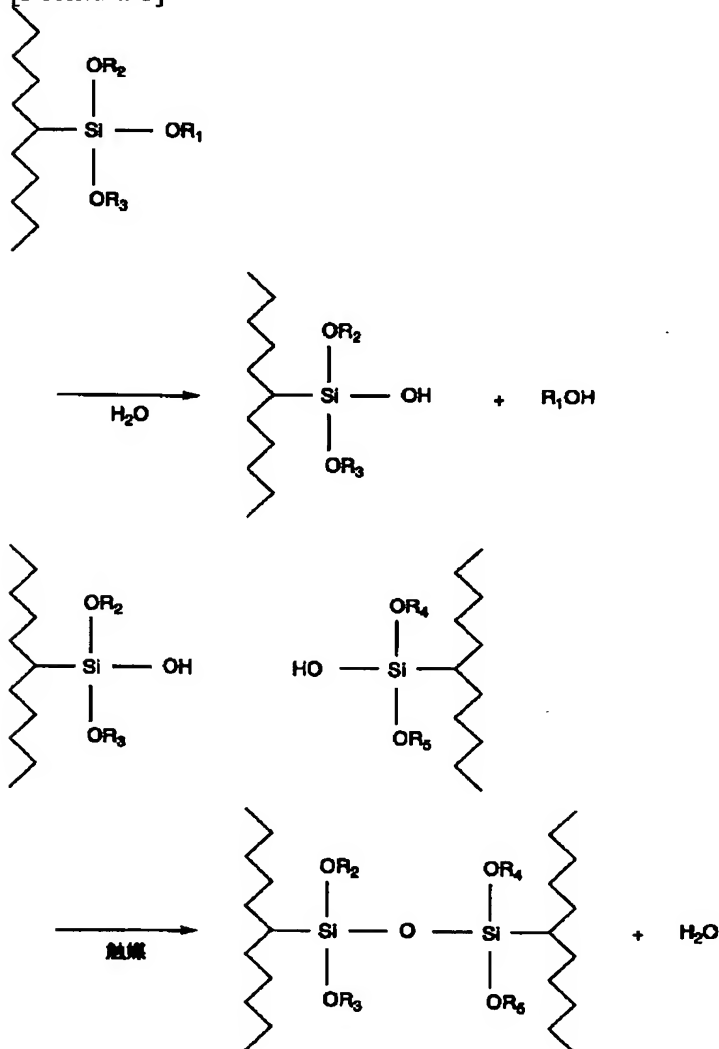
[0019] By making a macromolecule matrix and a low-molecular organic compound into the structure of cross linkage, a configuration is held by the macromolecule matrix, condensation of the low-molecular organic compound which repeats melting-coagulation at the time of actuation, and a segregation are controlled, and it is thought that the property stability of an organic positive thermistor improves. Moreover, a coupling agent forms a chemical bond not only between bridge formation of the above-mentioned organic matrix but between organic - inorganic materials, and is considered that big effectiveness is shown in refining of the interface. By processing a thermoplastic macromolecule matrix, a low-molecular organic compound, and the mixture of a conductive particle by the silane system coupling agent, the interface of a macromolecule matrix-conductivity

particle, the interface of a low-molecular organic compound-conductivity particle, the interface of a macromolecule matrix-metal electrode, and the interface of a low-molecular organic compound-metal electrode are strengthened, and it is thought that it has contributed to the stable improvement in a property further.

[0020] In this invention, a coupling agent is graft-ized by a thermoplastic macromolecule matrix and the low-molecular organic compound through the radical which has a carbonaceous double bond ( $C=C$ ), and a bridge is constructed over it by dealcoholization and dehydration condensation under existence of water after that. The reaction formula is shown below.

[0021]

[Formula 1]



[0022] As the bridge formation approach, there are a chemistry cross-linking method which uses organic peroxide, and another radiation-induced crosslinking method by electron beam irradiation. However, a chemistry cross-linking method must be heat-treated at temperature still higher than the melting point of the macromolecule matrix after shaping, it is difficult to hold a configuration and a component may heat-deteriorate. It is expensive, when moreover especially a component is thick, it is difficult for a radiation-induced crosslinking method to fully construct a bridge to the interior, and uniform bridge formation is difficult for it.

[ of equipment ]

[0023] In addition, performing silane bridge formation processing is already proposed. By the system not using a low-molecular organic compound, the half-conductivity constituent with which 15 - 50wt% conductive carbon is distributed for the gel molar fraction by homogeneity in 60% or more of silyl denaturation polyolefine by which water bridge formation was carried out is indicated by JP,59-60904,A, for example. The resistor

which has the polymer by which water bridge formation was carried out, and the PTC property that conductive powder is specifically distributed by the organic silane denaturation polymer is indicated by JP,4-68501,A. The polymer (polyolefine system resin) and the conductive powder (carbon black) by which water bridge formation is not carried out are mixed, and after adding the polymer (polyethylene which has an activity silane radical) by which water bridge formation is carried out further and mixing, the resistor which has the PTC property which carried out water bridge formation is indicated by JP,4-157701,A.

[0024] However, polyolefine is a working substance excluding a low-molecular organic compound, and these have a high operating temperature above 100 degrees C. Moreover, since carbon black etc. is used for the conductive particle, room temperature specific resistance is as high as 101 or more ohm cm, resistance rate of change is about 2-5 figures, and a property is inadequate [ rate of change ]. In addition, in these official reports, there is no suggestion about the stability of a property.

[0025] Moreover, the crystalline polymer resin of a polyolefine system, a silane system compound, organic peroxide, a stabilizer and conductive powder, and the heating element resin constituent that specifically consists of carbon are indicated by JP,3-74481,B. Under existence of a stabilizer, organic peroxide is used for a crystalline polymer, the chemical bond of the silane system compound is carried out to it, and further, in the functional group and chemical bond on the front face of carbon, formation or compatibility is raised, carbon is unevenly distributed, and while preventing that resistance changes, since an adhesive property with an electrode material also improves when a silane system compound carries out a chemical bond, it is supposed that the stability of a property is high. Conductive powder is distributed, into a crystalline polymer constituent, a conductive constituent is prepared and a bridge is constructed, and this bridge formation object is ground in JP,4-345785,A, surface treatment is carried out to it by the silane coupling agent, and the resistor with the forward temperature coefficient of resistance which carried out mixed distribution of this at the crystalline polymer constituent is indicated. Since a chemical bond is formed between binder macromolecule metallurgy group electrodes by applying a silane coupling agent to a particle-like conductivity constituent, association will become firm, resistance buildup of a heating element is controlled for formation of the electric conduction pass at the time of energization, and control of generating of the crack in the conductive fine particles resulting from the thermal expansion by energization generation of heat, and it is supposed that the life of a heating element can be lengthened.

[0026] However, these things are only performing surface treatment to the last, the improvement in property stability is small and the property by which the direction of the thing of this invention was stabilized over the long period of time is acquired. Moreover, it is unknown how much an early property is shown to an example by neither of above-mentioned official report, but degradation by trial is. Moreover, carbon is used as conductive powder and low initial resistance and big resistance rate of change are not reconciled like this invention. Moreover, crystalline polymer resin is a working substance excluding a low-molecular organic compound, and these things also have a high operating temperature above 100 degrees C.

[0027] Furthermore, it is proposed that the system using a low-molecular organic compound also performs silane bridge formation processing.

[0028] Water bridge formation form polyolefine and the self-temperature control mold heating element component which specifically comes to blend a conductive filler and a low-molecular-weight polyolefine wax with organic silane denaturation polyolefine are indicated by JP,1-231284,A. Water bridge formation form polyolefine and the \*\* style component which specifically comes to blend a conductive filler and a low-molecular-weight polyolefine wax with organic silane denaturation polyolefine are indicated by JP,9-69410,A. However, these things are mixing the low-molecular-weight polyolefine wax to water bridge formation form polyolefine, and have not made the macromolecule matrix and the low-molecular organic compound the structure of cross linkage like this invention. Therefore, the improvement in the stability of a property is dramatically small, and the thing of this invention cannot maintain a high property over a long period of time. In addition, in these official reports, there is no suggestion about the stability of a property. Moreover, in JP,9-69410,A, carbon black, graphite, carbon fiber, and metal powder (for example, nickel) are used for the conductive filler, and reference is not made about the conductive particle which has the projection of the letter of a spike. Therefore, although the room temperature specific resistance of this thing is as low as 10-1 - 100ohm cm, it does not have property that resistance rate of change is as small as triple or less figures, and it is sufficient to use for an overcurrent protection component or a thermo sensor. In JP,1-231284,A, since carbon black is



used for the conductive filler, room temperature specific resistance is as high as  $10^1 - 10^2 \Omega \text{ cm}$ , resistance rate of change is as small as figures triple [ about ], and it does not have sufficient property. Moreover, organic silane denaturation polyolefine and a low-molecular-weight polyolefine wax are working substances, and since operating temperature also uses the wax with a melting point of 100-160 degrees C, it is higher than the thing of this invention, and as for these, it does not operate at less than 100 degrees C. In this invention, since the melting point is using only low-molecular 40-degree-C or more less than 100-degree C organic compound as the working substance, operating temperature is low made with less than 100 degrees C.

[0029]

[Embodiment of the Invention] Hereafter, this invention is explained to a detail. The organic positive thermistor of this invention carries out bridge formation processing of such mixture including the conductive particle to which a thermoplastic macromolecule matrix and the melting point have the projection of a less than 100-degree C low-molecular organic compound 40 degrees C or more and the letter of a spike by the silane system coupling agent which has a vinyl group or (meta) an acryloyl radical, and an alkoxy group.

[0030] In order that the melting point of a thermoplastic macromolecule matrix may prevent floating by fusion of the low-molecular organic compound at the time of actuation, deformation of an element assembly, etc., it is desirable that it is higher than the melting point of a low-molecular organic compound, and its 30-degree-C or more thing high 110 degrees C or less is preferably desirable more preferably 30 degrees C or more. Moreover, as for the melting point of a thermoplastic macromolecule matrix, it is desirable that it is usually 70-200 degrees C.

[0031] Crystallinity or amorphism nature is sufficient as a thermoplastic giant-molecule matrix. Polyethylene, Poly alkyl acrylate, such as an ethylene-vinyl acetate copolymer and polyethylacrylate, Polyolefines, such as poly alkyl (meta) acrylate, such as poly methyl (meta) acrylate, Polyvinylidene fluoride, polytetrafluoroethylene, poly hexafluoropropylene, Fluorine system polymers, such as these copolymers, a polyvinyl chloride, a polyvinylidene chloride, Halogen system polymers, such as chlorine-based polymers, such as a chlorination polyvinyl chloride, chlorinated polyethylene, chlorination polypropylene, and these copolymers, polystyrene, thermoplastic elastomer, etc. are mentioned. Polyolefine may be a copolymer. concrete -- high-density-polyethylene (for example, [trade name high ZEKKUSU 2100JP (product made from Mitsui petrochemistry), trade name Marlex6003 (made in Philips)], etc.), and low-density-polyethylene [-- for example ], such as a trade name LC 500 (Japan Polychem make) and trade name DYNH-1 (made in Union Carbide), and medium-density-polyethylene [-- for example ], such as trade name 2604M (gulf company make), and ethylene-ethyl acrylate copolymer [-- for example ], such as a trade name DPD 6169 (made in Union Carbide), and ethylene-acetic-acid copolymer [-- for example ], such as the trade name nova tech EVALV241 (Japan Polychem make), and polyvinylidene fluoride [-- for example ], such as a trade name Kynar711 (Elf Atochem make), a vinylidene fluoride-tetrafluoroethylene-hexafluoropropylene copolymer [the for example, trade name KynarADS (Elf Atochem make) etc.], etc. are mentioned. As for the weight average molecular weight Mw of such a thermoplastic macromolecule, it is desirable that it is 10,000 to about 5 million.

[0032] As a thermoplastic macromolecule matrix, it is desirable to use polyolefine, and it is desirable to use high density polyethylene especially. A consistency says a three or more 0.942 g/cm thing, and is manufactured by coordinated anionic polymerization using a transition metal catalyst under the inside of dozens of or less atmospheric pressures, and low voltage, and high density polyethylene is a straight chain-like.

[0033] the melt flow rate (MFR) defined by ASTM D1238 of high density polyethylene -- 3.0 -- especially 1.5g / 10 min or less are desirable g/10 or less min. If MFR is higher than this, the inclination for melt viscosity to be too low and to be inferior to the stability of a property will be seen. Although there is especially no minimum of MFR, they are usually 0.1g / 10min extent.

[0034] Although it is not cared about even if only one sort is used for the thermoplastic macromolecule matrix of this invention, and it uses two or more sorts together, it is desirable to use only MFR3.0g / high density polyethylene of 10 or less min.

[0035] The low-molecular organic compound used for this invention is the crystalline substance of 200-800 preferably to about 1000 molecular weight, and that whose melting point mp is a solid-state in ordinary temperature (temperature of about 25 degrees C) although there will be especially no limit if it is 40 degrees C or more less than 100 degrees C is desirable.

[0036] As a low-molecular organic compound, there are waxes (specifically petroleum system waxes, such as



paraffin wax and a micro crystallin wax, a vegetable system wax, an animal system wax, a natural wax like a mineral system wax, etc.), fats and oils (what is specifically called a fat or solid-state fat), etc. The component of a wax or fats and oils A hydrocarbon (-- concrete -- the straight chain hydrocarbon of a with a carbon numbers of 22 or more alkane system etc. --) -- a fatty acid (-- concrete -- the fatty acid of the straight chain hydrocarbon of a with a carbon numbers of 12 or more alkane system etc. --) -- fatty acid ester The methyl ester of the saturated fatty acid specifically obtained from with a carbon numbers of 20 or more saturated fatty acid and lower alcohol, such as methyl alcohol, etc. and (fatty-acid) amides (-- concrete -- unsaturated fatty acid amides, such as oleic amide and an erucic-acid amide, etc. --), although it is fatty amine (specifically with a carbon numbers of 16 or more aliphatic series primary amine), higher alcohol (specifically with a carbon numbers of 16 or more n-alkyl alcohol), etc. These very thing can be independently used as a low-molecular organic compound. As a low-molecular organic compound, a petroleum system wax is desirable.

[0037] These low-molecular organic compounds are marketed and a commercial item can be used for them as it is.

[0038] In this invention, since operating temperature aims at the less than 100-degree C thermistor, as a low-molecular organic compound, the melting point mp uses 40-degree-C or more thing it is [ thing ] less than 100 degrees C. As such a thing, it is paraffin wax (for example, 49-52 degree C of tetracosane C<sub>24</sub>H<sub>50</sub>;mp(s)). Hexa thoria KONTAN C<sub>36</sub>H<sub>74</sub>;mp73 degree C, trade name HNP-10(NIPPON SEIRO CO., LTD. make);mp75 degree C, Micro crystallin waxes, such as HNP-3(NIPPON SEIRO CO., LTD. make);mp66 degree C for example, trade name Hi-Mic-1080(NIPPON SEIRO CO., LTD. make);mp -- 83 degree C Hi-Mic-1045 (NIPPON SEIRO CO., LTD. make);mp70 degree C, Hi-Mic2045(NIPPON SEIRO CO., LTD. make);mp64 degree C, Hi-Mic3090(NIPPON SEIRO CO., LTD. make);mp89 degree C, SERATTA 104(Nippon Oil purification company make);mp96 degree C, 155 micro wax (the Nippon Oil purification company make); mp70 degree C etc., a fatty acid (for example, behenic acid (Nippon Fine Chemical make);mp81 degree C and stearin acid (Nippon Fine Chemical make);mp -- 72 degree C) Palmitic acid (Nippon Fine Chemical make); mp64 degree C etc. has fatty acid ester (for example, arachin acid methyl ester (made in formation [ Tokyo ]);mp48 degree C etc.), a fatty-acid amide (for example, oleic amide (Nippon Fine Chemical make);mp76 degree C), etc. Moreover, what mixed the micro crystallin wax in the combination wax which blended resin with paraffin wax, or this combination wax, and made the melting point 40 degrees C or more less than 100 degrees C can be used preferably.

[0039] One sort or two sorts or more can be chosen and used for a low-molecular organic compound with operating temperature etc.

[0040] The conductive particle which has the projection of the letter of a spike used for this invention is formed from one piece and a primary particle with the projection with one sharp piece, and the projection of the letter of a spike of the shape of \*\*\*\* of the height of 1 / 3 - 1/50 of particle size recognizes [ the particle ] two or more (usually 10-500 pieces) existence at one particle. The construction material has a metal, especially desirable nickel, etc.

[0041] Although one piece and one piece may be the fine particles which exist according to an individual, as for such a conductive particle, it is desirable that about 10-1000 primary particles stand in a row in the shape of a chain, and form the aggregated particle. A primary particle may exist in a chain-like thing in part. As a former example, there is spherical nickel powder with the projection of the letter of a spike, and it is a trade name INCO. Type It is marketed as 123 nickel powder (parakeet company make), and the mean particle diameter is 3-7 micrometers. Extent and an apparent consistency are about three 1.8 - 2.7 g/cm, and specific surface area is about [ 0.34-0.44m ] 2/g.

[0042] Moreover, as an example of the latter used preferably, there is filament-like nickel powder and it is a trade name INCO. Type It is marketed as 210, 255, 270, and 287 nickel powder (parakeet company make), among these is INCO. Type 255, 270, and 287 are desirable. And the mean particle diameter of the primary particle is 0.1 micrometers preferably. It is or more 0.5 4.0-micrometer or less extent more preferably above. Among these, 1.0 or more micrometers [ 4.0 ] or less are the most desirable, and the mean particle diameter of a primary particle is the mean particle diameter of 0.1 micrometers to this. A less than 1.0-micrometer thing may be mixed 50 or less % of the weight above. Moreover, an apparent consistency is about three 0.3 - 1.0 g/cm, and specific surface area is about [ 0.4-2.5m ] 2/g.

[0043] In addition, the mean diameter in this case is measured by the fish subsieve method.

[0044] Such a conductive particle is indicated by JP,5-47503,A and the U.S. Pat. No. 5378407 description.

[0045] As a conductive particle moreover, besides the conductive particle which has the projection of the letter of a spike Carbon black, graphite, a carbon fiber, metallic-coating carbon black, Carbon system conductivity particles, such as graphite-ized carbon black and a metallic-coating carbon fiber, Metal particles, such as the shape of a globular shape and a flake, and fibrous, dissimilar metal coat metal particles (silver coat nickel etc.), tungsten carbide, titanium nitride, zirconium nitride, titanium carbide, titanium boride, and silicification -- the conductive potassium titanate whisker indicated by ceramic system conductivity particles, such as molybdenum, and JP,8-31554,A, and the 9-27383 official report may be added. As for such a conductive particle, it is desirable to carry out to 25 or less % of the weight which has the projection of the letter of a spike of a conductive particle.

[0046] The mixing ratio of the thermoplastic macromolecule matrix in this invention and a low-molecular organic compound is a weight ratio, and it is desirable that it is a 0.2 to 4 times as many low-molecular organic compound as this to the thermoplastic macromolecule 1. If this mixing ratio becomes small and the amount of a low-molecular organic compound decreases, resistance rate of change will become that it is sufficiently hard to be obtained. If it becomes large to objection and the amount of a low-molecular organic compound increases, in case a low molecular weight compound fuses, an element assembly will deform greatly, and also mixing with a conductive particle becomes difficult. As for a conductive particle, it is desirable to carry out by 2 to 5 times the sum total weight of a macromolecule matrix and a low-molecular organic compound. If this mixing ratio becomes small and the amount of a conductive particle decreases, it becomes impossible to make sufficiently low room temperature resistance at the time of un-operating. If the amount of a conductive particle increases reversely, big resistance rate of change will become is hard to be acquired, and uniform mixing will become difficult, and reproducible resistance will become is hard to be acquired.

[0047] What is necessary is just to perform kneading at the temperature more than the melting point of a thermoplastic macromolecule matrix (preferably temperature with a melting point of +5-40 degrees C). What is necessary is just to knead about 5 to 90 minutes with a mill etc. that what is necessary is to just specifically be based on a well-known approach. Moreover, a thermoplastic macromolecule and a low-molecular organic compound may be beforehand dissolved in melting mixing or a solvent, and you may mix. And a silane system coupling agent is added in this kneading object, and bridge formation processing is carried out.

[0048] A silane system coupling agent can be condensed by dealcoholization and dehydration, and has in a molecule an inorganic oxide, the alkoxy group in which a chemical bond is possible, and the vinyl group or (meta) acryloyl radical which carries out a chemical bond to an organic material with compatibility. As a silane system coupling agent, C=C joint content trialkoxysilane is desirable.

[0049] The direction of an alkoxy group with few carbon numbers is desirable, and a methoxy group and especially its ethoxy radical are desirable. The radical containing C=C association is a vinyl group or (meta) an acryloyl radical, and its vinyl group is desirable. These radicals may be combined with Si through the chain of carbon numbers 1-3, even if it has combined with direct Si.

[0050] As for a silane system coupling agent, what is a liquid in ordinary temperature is desirable.

[0051] Specifically as a silane system coupling agent, vinyltrimetoxysilane, vinyltriethoxysilane, a vinyl tris (beta-methoxyethoxy) silane, gamma-(meta) acryloxypropyltrimethoxysilane, gamma-(meta) acryloxypropyltriethoxysilane, gamma-(meta)acryloxypropylmethyldimethoxysilane, gamma-(meta) acryloxypropylmethyldiethoxysilane, etc. are mentioned. Especially, vinyltrimetoxysilane and vinyltriethoxysilane are desirable.

[0052] After dropping 0.1 - 5% of the weight of the silane system coupling agent of the sum total weight of a thermoplastic macromolecule and a low-molecular organic compound into a thermoplastic macromolecule matrix, a low-molecular organic compound, and the kneading object of a conductive particle and often mixing, water bridge formation of the coupling processing is carried out. When a coupling agent is more nearly little than this, the effectiveness of bridge formation processing becomes small, and when abundant, change is no longer looked at by the effectiveness. When using a silane system coupling agent with a vinyl group, it is 5 - 20% of the weight of organic peroxide of coupling agent, 2 [ for example, ], and 2-G (tert-butyl peroxide) butane, dicumyl peroxide, 1, and 1-G tert-butyl peroxide. - Both 3, 3, and 5-trimethyl cyclohexanes etc. are made to mix, and graft-ization is performed to the organic substance, i.e., a thermoplastic macromolecule and a low-molecular organic compound, through a vinyl group. Addition of a silane system coupling agent is

performed after a thermoplastic macromolecule, a low-molecular organic compound, and a conductive particle are enough kneaded by homogeneity.

[0053] A kneading object carries out press molding and carries out bridge formation processing to the sheet configuration of predetermined thickness under existence of water. Specifically, it carries out by dipping a Plastic solid for 6 to 8 hours in warm water, using metal carboxylate, such as a dibutyl tin JIRAU rate, a dioctyl tin JIRAU rate, acetic-acid tin, oct acid tin, and oct acid zinc, as a catalyst. Moreover, a catalyst can be kneaded to a thermistor element assembly and a bridge can also be constructed downward whenever [ high-humidity/temperature ]. As a catalyst, it is desirable to use a dibutyl tin JIRAU rate especially. In order to raise the stability of properties, such as repeat actuation, as for bridge formation temperature, it is desirable to carry out below with the melting point of a low-molecular organic compound. And after carrying out bridge formation processing, a Plastic solid is dried, thermocompression bonding of the metal electrodes, such as Cu and nickel, is carried out, and it considers as a thermistor component.

[0054] The organic positive thermistor of this invention has the low initial resistance at the time of un-operating, it is  $10^{-2}$  - 100ohm cm extent, and its resistance rate of change which lasts from the time of un-operating at the time of actuation is [ the room temperature resistivity has the steep standup of the resistance at the time of actuation, and ] as large as 6 or more figures. Moreover, even if it passes in 80-degree-C80%RH more than 500 hour (Tokyo 20 years or more and Naha ten years or more of humidity life), the property hardly deteriorates.

[0055] Moreover, in order to prevent the heat deterioration of a macromolecule matrix and a low-molecular organic compound, an antioxidant can also be mixed in the organic thermistor of this invention, and phenols, organic sulfur, and FOSU fights (organic phosphorus system) are used for it.

[0056] Moreover, an inorganic nitride, a magnesium oxide, etc. which are indicated by the silicon nitride indicated by JP,57-12061,A, a silica, an alumina, clay (a mica, talc, etc.), the silicon indicated by JP,7-77161,B, silicon carbide, silicon nitride, beryllia, a selenium, and JP,5-217711,A may be added as a right pyroconductivity additive.

[0057] On the titanium oxide indicated by JP,5-226112,A for the improvement in endurance, ferrous oxide, a zinc oxide, a silica, magnesium oxide, an alumina, chromic oxide, a barium sulfate, a calcium carbonate, a calcium hydroxide, lead oxide, the inorganic solid-state of the high specific inductive capacity indicated by JP,6-68963,A, and a concrete target, barium titanate, strontium titanate, a niobic acid potassium, etc. may be added.

[0058] The boron carbide indicated by JP,4-74383,A for the withstand voltage improvement may be added.

[0059] The hydration titanate-acid alkali indicated by JP,5-74603,A for the improvement on the strength, the titanium oxide indicated by JP,8-17563,A, an iron oxide, a zinc oxide, a silica, etc. may be added.

[0060] the alkali halide indicated by JP,59-10553,B as a crystalline-nucleus agent, melamine resin, the benzoic acid indicated by JP,6-76511,A, a JIBEN zylidene sorbitol, a benzoic-acid metal salt, the talc indicated by JP,7-6864,A, a zeolite, a JIBEN zylidene sorbitol, the sorbitol derivative (gelling agent) indicated by JP,7-263127,A, and asphalt -- phosphoric-acid screw (4-t-buthylphenyl) sodium etc. may be added further.

[0061] As an arc accommodation control agent, the alumina indicated by JP,4-28744,B, a magnesia hydrate, the metal hydrate indicated by JP,61-250058,A, silicon carbide, etc. may be added.

[0062] As a metal damage inhibitor, IRUGA NOx MD 1024 (Ciba-Geigy make) indicated by JP,7-6864,A may be added.

[0063] Moreover, the Lynn system compounds, such as 3 oxidization 2 antimony indicated by JP,61-239581,A, an aluminum hydroxide, a magnesium hydroxide indicated by JP,5-74603,A, an organic compound (a polymer is included) containing halogens, such as 2 and 2-screw (4-hydroxy - 3, 5-dibromo phenyl) propane and polyvinylidene fluoride (PVDF), and ammonium phosphate, etc. may be further added as a flame retarder.

[0064] Besides these, zinc sulfide, basic magnesium carbonate, an aluminum oxide, a calcium silicate, a magnesium silicate, aluminosilicate clay (a mica, talc, a kaolinite, montmorillonite, etc.), glass powder, a glass flake, a glass fiber, a calcium sulfate, etc. may be added.

[0065] As for these additives, it is desirable that it is 25 or less % of the weight of the sum total weight of a macromolecule matrix, a low-molecular organic compound, and a conductive particle.

[0066]

[Example] Hereafter, the example of this invention is shown with the example of a comparison, and this

invention is explained concretely.

Filament-like nickel powder (the product made from INCO, trade name Type255 nickel powder) was used as a <example 1> giant-molecule matrix as a micro crystallin wax (the NIPPON SEIRO CO., LTD. make, Hi-Mic - 1080; melting point of 83 degrees C), and a conductive particle as high density polyethylene (the Japan Polychem make, trade name HY540;MFR1.0g/10min, melting point of 135 degrees C), and a low-molecular organic compound. The mean particle diameter of a conductive particle is 2.2-2.8 micrometers. An apparent consistency is 0.5 - 0.65 g/cm<sup>3</sup>, and specific surface area is 0.68m<sup>2</sup>/g.

[0067] High density polyethylene and its nickel powder of 4 time weight were kneaded for 5 minutes at 150 degrees C among the mill. And the nickel powder of 4 time weight of the wax of 1.5 time weight of high density polyethylene and a wax was added further, and it kneaded. As a silane system coupling agent, as polyethylene, 1.0% of the weight of the vinyltriethoxysilane (the Shin-Etsu Chemical make, product name KBE 1003) of the sum total weight of a wax, and organic peroxide, 2 and 2-G (tert-butyl peroxide) butane (the Kayaku AKZO make, product name Trigonox D-T50) of 20% of the weight of vinyltriethoxysilane was dropped into the kneading object, and was kneaded for 60 minutes.

[0068] This kneading object was fabricated at 150 degrees C with the heat press machine with a thickness of 1.1mm in the shape of a sheet. And this sheet was dipped in the 20 % of the weight (made in formation [ Tokyo ]) emulsion water of dibutyl tin JIRAU rates, and bridge formation processing was performed at 65 degrees C for 8 hours.

[0069] It is 30 micrometers in thickness about both sides after drying this sheet that carried out bridge formation processing. It inserted with nickel foil electrode, nickel foil was stuck to the sheet by pressure at 150 degrees C using the heat press machine, and the cast with a thickness of 1mm was obtained on the whole. And this was pierced to discoid with a diameter of 10mm, and the thermistor component was obtained. The sectional view of this thermistor component is shown in drawing 1 . As shown in drawing 1 , a thermistor component puts the thermistor element assembly 12 which is a kneading molding sheet containing a low-molecular organic compound, a macromolecule matrix, and a conductive particle between the electrodes 11 formed from nickel foil.

[0070] This component was heated within the thermostat and it cooled, and at predetermined temperature, resistance was measured by 4 terminal method and the temperature-system head curve was obtained. This result is shown in drawing 2 .

[0071] Room temperature (25 degrees C) resistance was 2.0x10 to 3 ohm (1.6x10-2ohm cm), rapid lifting of resistance was seen near 75 degree C, the maximum resistance was set to 1.6x10<sup>5</sup> ohms (1.3x10<sup>6</sup>ohm cm), and resistance rate of change was 7.9 figures.

[0072] the constant temperature which set this component as 80-degree-C80%RH -- it was left in the constant humidity chamber and the accelerated test was performed. The room temperature resistance and the resistance rate of change in each neglect time amount are shown in drawing 3 . The room temperature (25 degrees C) resistance of 500 hours after is 5.3x10 to 3 ohm (4.2x10-2ohm cm), resistance rate of change is 7.2 figures, and sufficient PTC property was maintained, without room temperature resistance and resistance rate of change hardly changing.

[0073] 80-degree-C80%RH and the accelerated test of 500 hours are absolute-humidity conversions, and will be equivalent to ten years or more of humidity life in Tokyo in Naha for 20 years or more. Count to the life under 25-degree-C60%RH conditions under 80-degree-C80%RH conditions from a life is made into an example, and absolute-humidity conversion are explained. The absolute humidity of 232.5 g/m<sup>3</sup> and 25-degree-C60%RH of the absolute humidity of 80-degree-C80%RH is 13.8 g/m<sup>3</sup>. It asks for an acceleration constant in the following formula as 2.

$(232.5/13.8)^{2.28385}$  -- in this case, if the lives under 80-degree-C80%RH conditions are 500hr(s), the life under 25-degree-C60%RH conditions will be set to 500hr(s)x283.85=141925hr\*\* 5914-day \*\* 16.2. The humidity of Tokyo and Naha carried out the absolute-humidity conversion of the monthly average relative humidity, and made the sum total annual humidity.

[0074] Paraffin wax (the NIPPON SEIRO CO., LTD. make, trade name HNP-10, melting point of 75 degrees C) was used as a <example 2> low-molecular nonaqueous solubility organic compound, and also the thermistor component was obtained like the example 1. And the temperature-system head curve was obtained like the example 1, and the accelerated test was performed.

[0075] The room temperature (25 degrees C) resistance of this component was  $2.0 \times 10$  to 3 ohm ( $1.6 \times 10$ -2ohm cm), rapid lifting of resistance was seen near 75 degree C, the maximum resistance was set to  $7.7 \times 10^6$  ohms ( $6.0 \times 10^7$ ohm cm), and resistance rate of change was 9.6 figures.

[0076] In the 80-degree-C80%RH accelerated test, the room temperature resistance of 500 hours after is  $6.2 \times 10$  to 3 ohm ( $4.9 \times 10$ -2ohm cm), resistance rate of change is 8.7 figures, and sufficient PTC property was maintained, without room temperature resistance and resistance rate of change hardly changing.

[0077] High density polyethylene (the Japan Polychem make, trade name HY420;MFR0.4g/10min, melting point of 134 degrees C) was used as a <example 3> giant-molecule matrix, and also the thermistor component was obtained like the example 1. And the temperature-system head curve was obtained like the example 1, and the accelerated test was performed.

[0078] The room temperature (25 degrees C) resistance of this component was  $4.0 \times 10$  to 3 ohm ( $3.1 \times 10$ -2ohm cm), rapid lifting of resistance was seen near 75 degree C, the maximum resistance was set to  $6.0 \times 10^4$  ohms ( $4.7 \times 10^5$ ohm cm), and resistance rate of change was 7.2 figures.

[0079] In the 80-degree-C80%RH accelerated test, the room temperature resistance of 500 hours after is  $7.5 \times 10$  to 3 ohm ( $5.9 \times 10$ -2ohm cm), resistance rate of change is 6.5 figures, and sufficient PTC property was maintained, without room temperature resistance and resistance rate of change hardly changing.

[0080] The <example 1 of comparison> silane system coupling agent and organic peroxide were not added, but bridge formation processing was not performed and also the thermistor component was obtained like the example 1.

[0081] The temperature-system head curve of this sample was obtained like the example 1. The room temperature (25 degrees C) resistance of this component was  $3.0 \times 10$  to 3 ohm ( $2.4 \times 10$ -2ohm cm), rapid lifting of resistance was seen near 75 degree C, the maximum resistance was set to  $8.2 \times 10^4$  ohms ( $6.4 \times 10^5$ -ohmcm), and resistance rate of change was 7.4 figures.

[0082] The accelerated test of this component was performed by 80-degree-C80%RH like the example 1. The room temperature resistance and the resistance rate of change in each neglect time amount are shown in drawing 4 . The room temperature resistance of 500 hours after increased 10 or more times from initial value by  $3.4 \times 10$  to 2 ohm ( $2.7 \times 10$ -1ohm cm), and resistance rate of change decreased to 5.4 figures.

[0083] The <example 2 of comparison> silane system coupling agent and organic peroxide were not added, but bridge formation processing was not performed and also the thermistor component was obtained like the example 2. And the temperature-system head curve was obtained like the example 1, and the accelerated test was performed.

[0084] The room temperature (25 degrees C) resistance of this component was  $2.0 \times 10$  to 3 ohm ( $1.6 \times 10$ -2ohm cm), rapid lifting of resistance was seen near 75 degree C, the maximum resistance was set to  $8.0 \times 10^7$  ohms ( $6.3 \times 10^8$ ohm cm), and resistance rate of change was 10.6 figures.

[0085] In the 80-degree-C80%RH accelerated test, the room temperature resistance of 500 hours after is 7.7 ohms ( $60.5$ ohm cm), resistance rate of change is 7.1 figures, and degradation with remarkable room temperature resistance and resistance rate of change was seen.

[0086] Low density polyethylene (the Japan Polychem make, trade name LC500;MFR4.0g/10min, melting point of 106 degrees C) was used as a <example 3 of comparison> giant-molecule matrix, and also the thermistor component was obtained like the example 1. And the temperature-system head curve was obtained like the example 1, and the accelerated test was performed.

[0087] The room temperature (25 degrees C) resistance of this component was  $3.0 \times 10$  to 3 ohm ( $2.4 \times 10$ -2ohm cm), rapid lifting of resistance was seen near 80 degree C, the maximum resistance became more than  $1.0 \times 10^9$ ohm ( $7.8 \times 10^9$ ohm cm), and resistance rate of change was 11 or more figures.

[0088] By the 80-degree-C80%RH accelerated test, although the maximum resistance of 100 hours after was  $1.0 \times 10^9$ ohms or more, room temperature resistance increased remarkably by  $7.0 \times 10$  to 1 ohm ( $5.5$ ohm cm).

[0089] High density polyethylene (the Japan Polychem make, trade name HJ360;MFR6.0g/10min, melting point of 131 degrees C) was used as a <example 4 of comparison> giant-molecule matrix, and also the thermistor component was obtained like the example 1. And the temperature-system head curve was obtained like the example 1, and the accelerated test was performed.

[0090] The room temperature (25 degrees C) resistance of this component was  $3.8 \times 10$  to 3 ohm ( $3.0 \times 10$ -2ohm cm), rapid lifting of resistance was seen near 75 degree C, the maximum resistance was set to  $8.0 \times 10^6$  ohms

( $6.3 \times 10^7$  ohm cm), and resistance rate of change was 9.3 figures.

[0091] Although the room temperature resistance of 500 hours after seldom changed by the 80-degree-C80% RH accelerated test by  $6.4 \times 10$  to 3 ohm ( $5.0 \times 10$ -2ohm cm), although resistance increased with the temperature rise, the transition point of the clear resistance seen in early stages was not accepted, but  $1.3 \times 10$  to 1 ohm and the rate of change from a room temperature of the resistance in 75 degrees C were 1.3 figures.

[0092] The room temperature resistance before and behind the accelerated test of examples 1-3 and the examples 1-4 of a comparison and resistance rate of change are summarized in a table 1. In addition, the melt flow rate (MFR) of a macromolecule matrix and the melting point mp of a low-molecular organic compound are written together.

[0093]

[A table 1]

表 1

	高分子マトリックス	低分子有機化合物(mp)	シラン 架橋	室温抵抗値(Ω)		抵抗変化率(桁)	
				初期値	加速試験後	初期値	加速試験後
実施例1	高密度ポリエチレン(MFR=1.0)	マイクロクリスタリンワックス(83℃)	有	$2.0 \times 10^{-3}$	$5.3 \times 10^{-3}$	7.9	7.2
実施例2	高密度ポリエチレン(MFR=1.0)	パラフィンワックス(75℃)	有	$2.0 \times 10^{-3}$	$6.2 \times 10^{-3}$	9.6	8.7
実施例3	高密度ポリエチレン(MFR=0.4)	マイクロクリスタリンワックス(83℃)	有	$4.0 \times 10^{-3}$	$7.5 \times 10^{-3}$	7.2	6.5
比較例1	高密度ポリエチレン(MFR=1.0)	マイクロクリスタリンワックス(83℃)	無	$3.0 \times 10^{-3}$	$3.4 \times 10^{-3}$	7.4	5.4
比較例2	高密度ポリエチレン(MFR=1.0)	パラフィンワックス(75℃)	無	$2.0 \times 10^{-3}$	7.7	10.6	7.1
比較例3	低密度ポリエチレン(MFR=4.0)	マイクロクリスタリンワックス(83℃)	有	$3.0 \times 10^{-3}$	$7.0 \times 10^{-1*}$	11 以上	9 以上*
比較例4	高密度ポリエチレン(MFR=6.0)	マイクロクリスタリンワックス(83℃)	有	$3.8 \times 10^{-3}$	$6.4 \times 10^{-3}$	9.3	—

\* 100時間後

[0094] In examples 1-3, even if it used vinyltrimetoxysilane for the silane system coupling agent, the result equivalent to the examples 1-3 using vinyltriethoxysilane was obtained, respectively. Moreover, the same effectiveness was acquired even if it used gamma-methacryloxypropyl trimethoxy silane and gamma-methacryloxypropyl triethoxysilane.

[0095]

[Effect of the Invention] According to this invention, sufficiently low room temperature resistance is obtained, the resistance rate of change at the time of actuation and un-operating is large, and it operates at less than 100 degrees C, and the hysteresis of a temperature-system head curve is small, adjustment of operating temperature is easy, and, moreover, an organic positive thermistor with high property stability can be offered.

[Translation done.]

\* NOTICES \*

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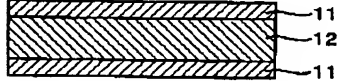
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- 3.In the drawings, any words are not translated.

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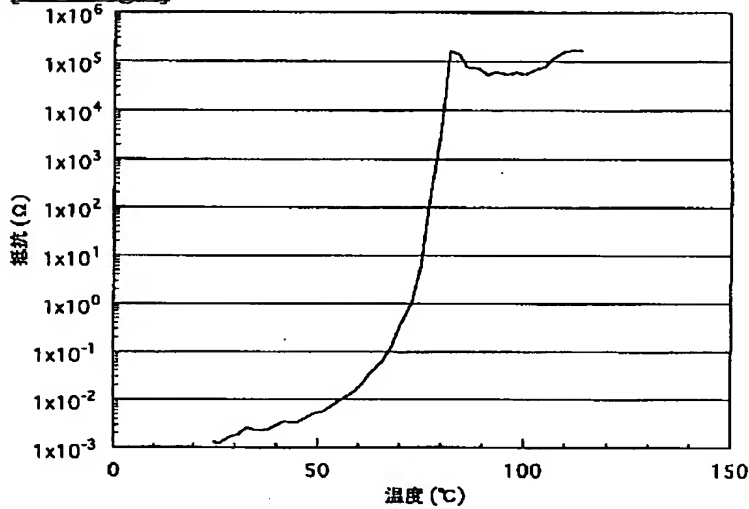
DRAWINGS

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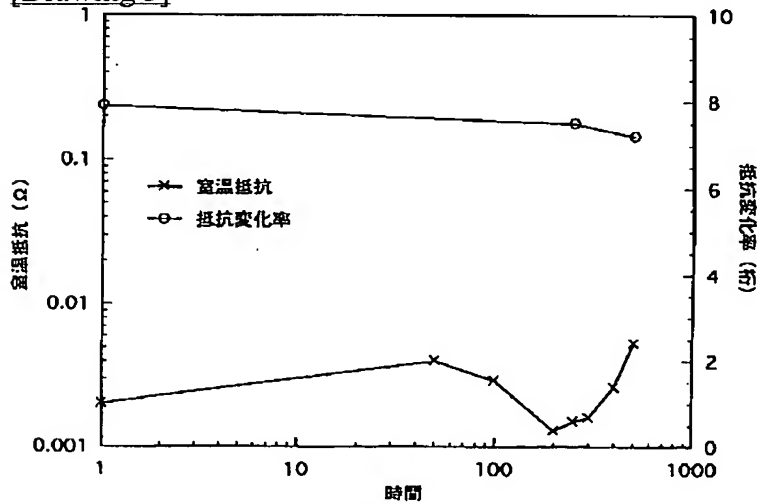
[Drawing 1]



[Drawing 2]

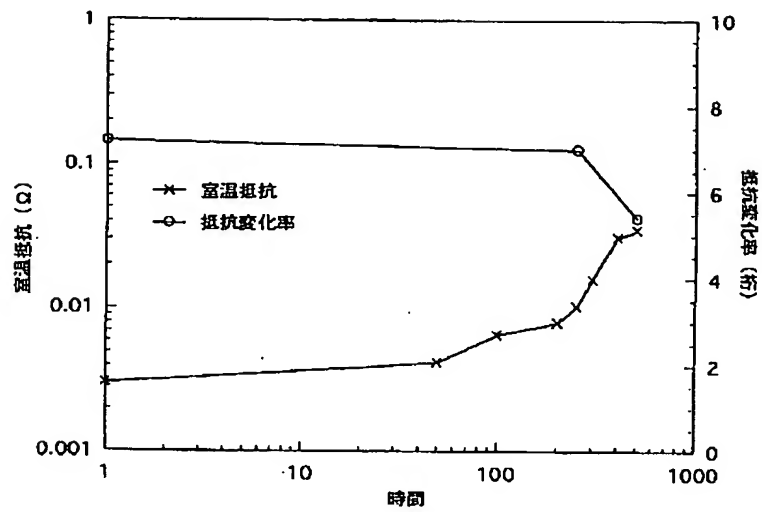


[Drawing 3]



[Drawing 4]





[Translation done.]